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Room temperature ferromagnetism in Cr-doped hydrogenated amorphous Si films

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Ferromagnetism above room temperature was observed in Cr-doped hydrogenated amorphous silicon films deposited by rf magnetron sputtering. Structure analysis reveals that films are amorphous without any detectable precipitates up to the solubility limit of 16 at.% Cr. Experimental results suggest that hydrogenation has a dramatic influence on magnetic properties, electrical conductivity, and carrier concentration in the thin films. Pronounced anomalous Hall effect and magnetization curve both suggest that the origin of the ferromagnetism may arise from percolation of magnetic polarons. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2946662]

Diluted magnetic semiconductor (DMS) is among the best candidates to realize spintronic devices with the potentials to manipulate both charge and spin degrees of freedom in one material.[1] One of the crucial criteria for its practical applications is to maintain robust ferromagnetism near/above room temperature. Even though fabrication of DMS has been achieved by doping transition metals into III–V semiconductors, such as $Ga_{1-x}Mn_xAs$ and $In_{1-x}Mn_xAs$, the Curie temperatures remain low. On the other hand, to enjoy the smooth integration with existing industry of modern electronics, doping crystalline Si (*c*-Si) and crystalline Ge (*c*-Ge) seems to kick off another route. For instance, Park *et al.*[2] reported that the Curie temperature of Mn_xGe_{1-x} deposited by molecule beam epitaxy increases linearly with the Mn concentration and goes up to 116 K at $x=0.035$. However, the reported Curie temperatures in *c*-Si and *c*-Ge based DMSs are rather scattered, ranging from 116 to 400 K in current literature.[2–6]

The challenge of turning Si/Ge crystalline hosts into DMS lies in the extremely low solubility of the magnetic dopants. This difficulty can be removed by using amorphous silicon (*a*-Si) that has a higher solubility. However, Liu *et al.*[7] investigated $Si_{1-x}Mn_x$:B thin films deposited by cosputtering and concluded that the as-deposited amorphous films are not ferromagnetic. Yu *et al.*[8] reported that amorphous $Si_{1-x}Mn_x$ ($x<0.09$) thin films grown by thermal deposition are also paramagnetic. We suspected that the null results for ferromagnetism may originate from the dangling bonds that trap dopants/carriers and deteriorate the conductivity and other desirable properties required for useful semiconductors.

The problem associated with dangling bonds can be cured by hydrogenation,[9] which has been widely used in many applications, such as thin film transistors in liquid crystal display and the *p-n* junction in solar cells. In this letter, we investigate transition-metal doped *a*-Si with or without hydrogenation. Remarkably, hydrogenated samples show robust ferromagnetism even above room temperature while the magnetic order is greatly suppressed without hydrogenation.

Cr-doped hydrogenated amorphous silicon (a-Cr_xSi_{1-x}:H) films were deposited by rf magnetron cosputtering onto a glass substrate using Si and Cr targets simultaneously. All films were deposited in a sputtering atmosphere of $Ar/H_2=80/20$ or pure Ar at room temperature. After deposition, we capped an Al layer on top of the films to prevent oxidation. The thickness of samples was fixed at 1 μm. The composition of a-Cr_xSi_{1-x} films was varied between $x=0\sim0.22$. The structure of the films was characterized by using x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM), while magnetic measurements were performed by the superconducting quantum interference device. Furthermore, the composition of samples was analyzed by a field-emission electron-probe microanalyzer. Finally, we also measured the Hall resistivity and the carrier concentration with the Van der Pauw configuration by a physical property measurement system (PPMS).

Figure 1(a) shows XRD patterns of a-Cr_xSi_{1-x}:H films at different dopings. At $x=0.18$, Cr (110) peak starts to appear, signaling the clustering above the solubility limit. Since the peak is absent at $x=0.14$, we assume an interpolated solubility limit of roughly 16 at.%. Figure 1(b) shows a typical HRTEM image of an a-$Cr_{0.14}Si_{0.86}$:H film. Although darker and brighter stripes are visible due to localized strain, no precipitate is observed. The inset diffraction pattern confirms

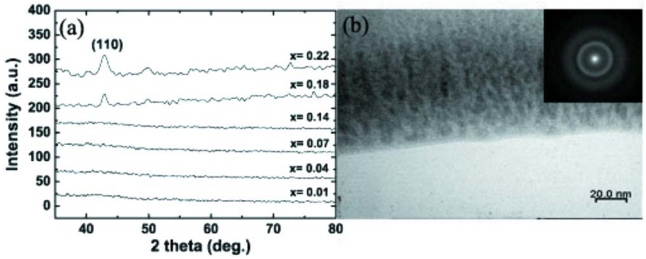

FIG. 1. (Color online) (a) XRD patterns from a-Cr_xSi_{1-x}:H samples with $x=0.01, 0.04, 0.07, 0.14, 0.18, 0.22$. (b) High-resolution TEM image of an a-$Cr_{0.14}Si_{0.86}$:H sample. The inset shows the corresponding selected-area electron diffraction pattern.

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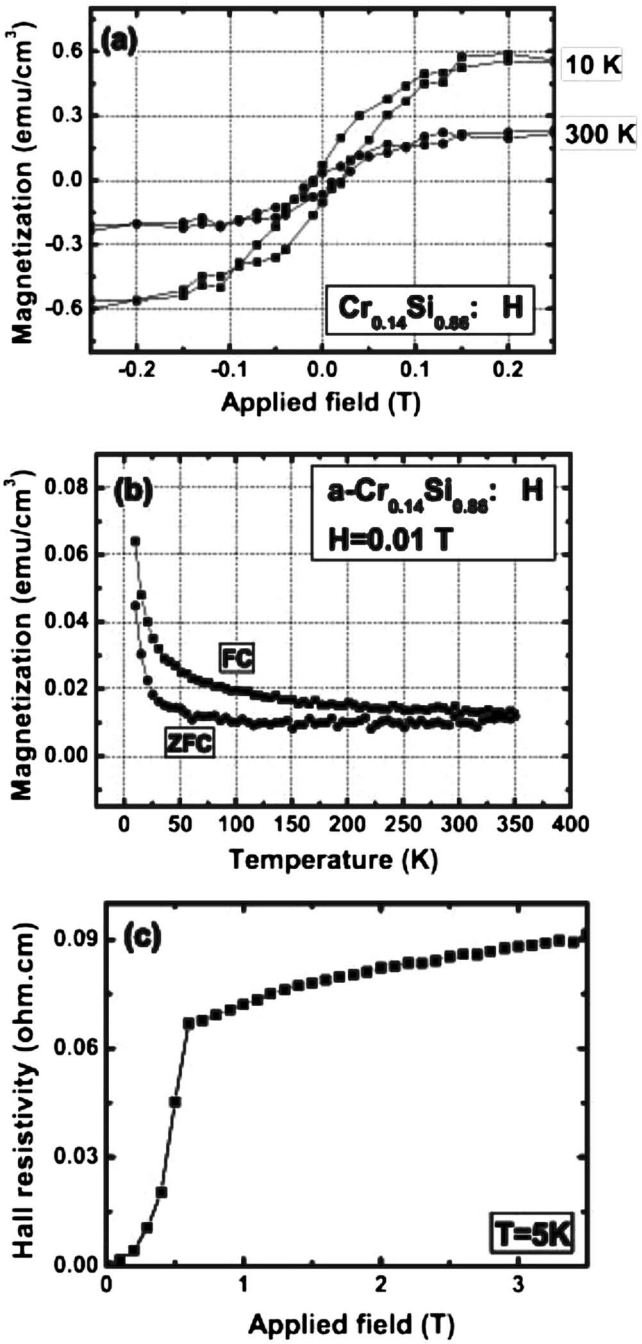

FIG. 2. (a) *M-H* curves of an a-$Cr_{0.14}Si_{0.86}$:H sample measured at 10 and 300 K, respectively. (b) Magnetization vs temperature in the presence/absence of a magnetic field of 100 Oe. (c) Anomalous Hall resistivity measured at 5 K.

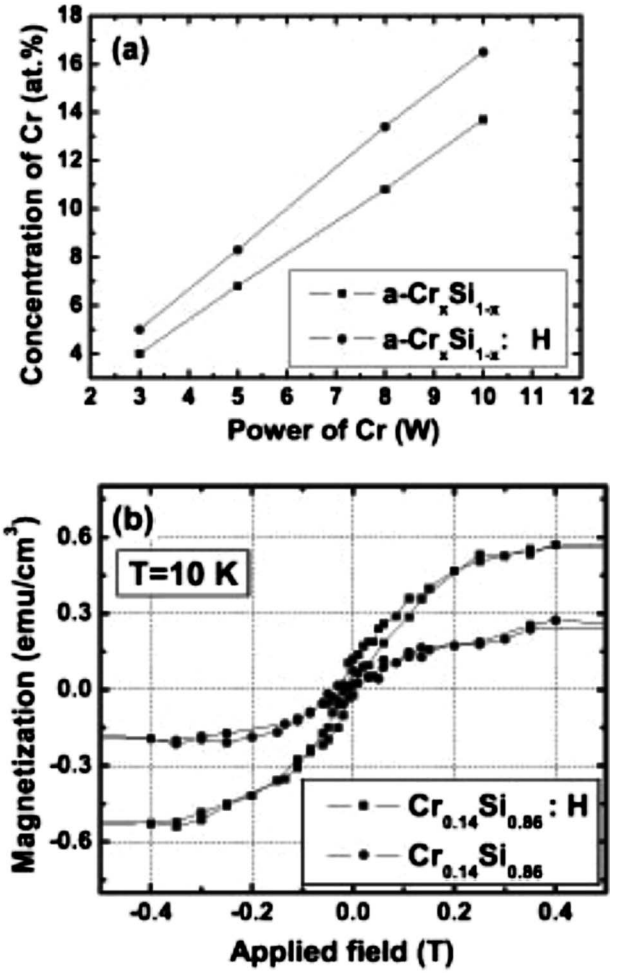

FIG. 3. (a) The effect of hydrogenation on the Cr concentration of a-Si films. (b) *M-H* curves measured at 10 K of a-Si films of the same Cr concentration with and without hydrogen.

the amorphous nature of the film. However, the magnetic moment associated with each Cr atom, 0.01 μB/Cr, is unexpectedly small. Since the film is protected by capped Al layer and magnetic Cr oxides are hard to form during sputter deposition, we suspect the small moment arises from the formation of clusters beyond the detection limit. The existence of such Cr clusters, being antiferromagnetic in nature, quench most Cr spins except the uncompensated moments from surface of the cluster,[10] effectively leading to a rather small moment per Cr atom. However, more experiments are necessary to pin down the exact cause.

We focus on the a-$Cr_{0.14}Si_{0.86}$:H sample with optimal magnetic properties. The ferromagnetism is clearly seen in Fig. 2(a) at both 10 and 300 K. The saturation magnetization is 0.23 emu/cm^3 and the coecivity is about 100 Oe at room temperature. Both the field-cooled (FC) and the zero-field-cooled (ZFC) magnetizations were measured from 350 K down to 10 K. The crossing point of FC and ZFC curves, serving as a rough estimate for Curie temperature, is clearly above room temperature. In addition, we also measured the Hall resistivity by PPMS in the presence of a perpendicular magnetic field of up to 3.5 T at T=5 K. As shown in Fig. 2(c), the anomalous Hall effect (AHE) is manifested, hinting the ferromagnetic order is mediated by charge carriers.

Note that the ferromagnetism sensitively depends on the magnetic doping. We have investigated samples with different doping levels x=0.11–0.22 and found that the magnetic order gets strengthened up to the optimal value x=0.14 and then suppressed by further doping due to the formation of antiferromagnetic clusters. This is consistent with the results reported by Peak *et al.*[11] for a-$Ge_{1-x}Cr_x$ samples.

Now we turn to the role of hydrogen passivation. Note that at the same sputtering power, Cr density is higher without hydrogenation, as shown in Fig. 3(a). The reduction in sputter yield of Cr is simply due to the presence of hydrogen in the working gases. For comparison, samples at the same Cr doping with and without hydrogenation are listed in Table I. One notices that the carrier concentration of the hydrogenated sample is one order of magnitude larger than that of the

TABLE I. Carrier concentration and conductivity of a-$Cr_{0.14}Si_{0.86}$ films with or without hydrogen.

Sample	Carrier concentration (cm^{-3})	Conductivity $(\Omega\,cm)^{-1}$
$Cr_{0.14}Si_{0.86}$:H	1.073×10^{22}	2.48×10^{2}
$Cr_{0.14}Si_{0.86}$	1.987×10^{21}	1.54×10^{2}

unhydrogenated, while the conductivity is only a factor of 2 larger. This implies that hydrogenation increases lots of charge carriers with low mobility. The increase in the carrier density coincides with stronger magnetic order in the hydrogenated sample as shown in Fig. 3(b). Hydrogenation enhances saturation magnetization of up to 100%. In fact, aside from the optimal doping of $x=0.14$, all other unhydrogenated a-Cr_xSi_{1-x} films show a diamagnetic behavior down to 10 K. Our findings explain the absence of ferromagnetism in transition-metal doped a-Si reported earlier[7,8] and establish the importance of hydrogenation to eliminate the dangling bonds in amorphous configuration.

Finally, we would like to explore the origin of the ferromagnetism. First, we assume that the holes are itinerant and estimate the Curie temperature by the Zener model within self-consistent Green's function approach.[12,13] However, with a reasonable exchange coupling between the itinerant and Cr spins ($J\sim100$ meV nm^3), the maximum Curie temperature never exceeds 100 K, far below that observed in our samples. We then turn to the percolation theory of magnetic polaron[14] with only one fitting parameter $a_B^3 n_h$, where a_B is the decay length of the magnetic polaron and n_h is the hole density. It is rather remarkable that the magnetization curve at optimal doping $x=0.14$ agrees with the theoretical prediction rather well as shown in Fig. 4. This scenario also agrees with the previous observations of the AHE and the presence of low-mobility carriers in the samples.

In conclusion, the Cr-doped hydrogenated a-Si has been found to demonstrate ferromagnetic order at room temperature. It is worth emphasizing that the ferromagnetism is either absent or strongly suppressed without hydrogen passivation. Only when dangling bonds in the sample are largely hydrogenated, will robust ferromagnetic order be observed.

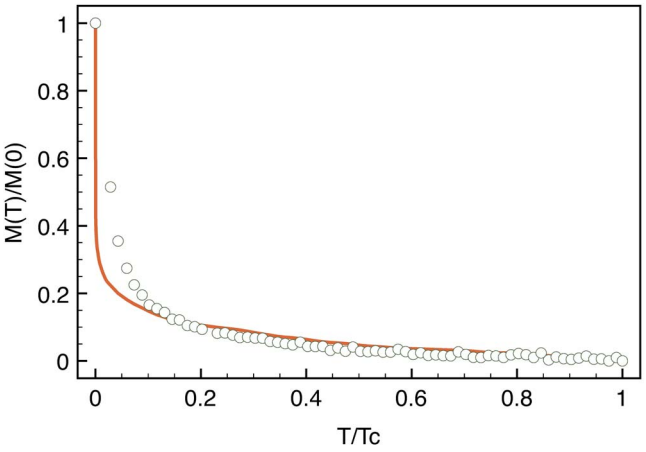

FIG. 4. (Color online) Magnetization curve for a-$Cr_{0.14}Si_{0.86}$:H sample (green dots) and the theoretical prediction (orange line) from magnetic polaron percolation with $a_B^3 n_h = 2.7\times10^{-5}$.

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